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(54) Flameproofing of Textiles

(57) A cellulosic textile is flameproofed by impregnating it with a solution containing a tetrakis hydroxymethyl phosphonium (THP) salt, a carbamic

acid derivative and a difunctional nitrogen-containing reactant compound such as dihydroxy dimethylol ethylene urea then heat-curing the impregnated textile which contains 15—30% by weight THP.

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## SPECIFICATION

### Flameproofing of Textiles

This invention relates to the flameproofing of textile fibres with resins produced by curing tetrakis hydroxymethyl phosphonium (hereinafter referred to as "THP") salts with nitrogen-containing compounds. The term 'flameproofing' as used herein means any treatment to render the fibres flame-retardant, notwithstanding that complete non-flammability may not be achieved. It has been commercial practice for many years to flameproof cellulosic fibres by this means. There have also been various suggestions for flameproofing other types of fibre, particularly polyester-cotton mixtures, i.e. mixtures in which the polyester is the major constituent, but these have not so far been commercially successful, (see Textile Chemist and Colorist (1969) Vol. 1 p. 366, especially at p. 368).

The curing of the THP system may be effected with the aid of heat, or ammonia. In an ammonia cured process the THP salt is applied to the fabric, usually after neutralisation to form THP hydroxide (THPOH) or condensation with urea to form a precondensate, and is then reacted with ammonia to form an insoluble polymer which is physically held within the cellulose fibres but which is not chemically attached to them. In the previously employed heat cured processes the fabric is treated with THP salt, plus varying amounts of neutralising agent, urea, and a thermosetting resin. On heating under suitable conditions the thermosetting resin binds the THP salt into a polymer and also binds this to the cellulose. The handle of a fabric treated with a heat cured finish is generally firmer and the strength weaker than when treated with an ammonia cured finish, and the latter is therefore usually preferred. However, the heat cured finish also improves the crease resistance of the fabric which the ammonia cured finish does not. The Textile Research Journal (1969) Vol. 39 p. 368, describes the development of a process using THPOH and trimethylol melamine with ammonia cure followed by heat cure.

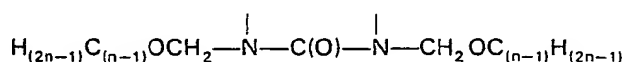
Our invention is based on the discovery that a heat-curing process to form a polymer derived from THP, a carbamic acid derivative such as urea and a di-functional reactant compound, gives good results in respect of flameproofing and durability of flame resistance, whilst the handle and strength of the treated fabric remain satisfactory.

A further important advantage of this process lies in the fact that it provides a satisfactory treatment for polyester-cotton mixtures. If the conventional ammonia-cured THP/urea treatment is used for such mixtures the cotton fibres become fully loaded with flame retardant polymer, but little becomes attached to the polyester, with the result that it is not possible to obtain a sufficiently great add-on of polymer on the fabric as a whole, to give adequate flameproofing. We have found that much higher uptake of flame retardant on the fabric can be obtained by using a mixture of THP, urea and a tri-functional thermosetting resin, but this is achieved by over loading the cotton and the handle of the treated fabric is too stiff. We have now further discovered that if the tri-functional thermosetting compound is replaced by a di-functional reactant one, a satisfactory flameproofing treatment for polyester-cotton mixtures can be obtained.

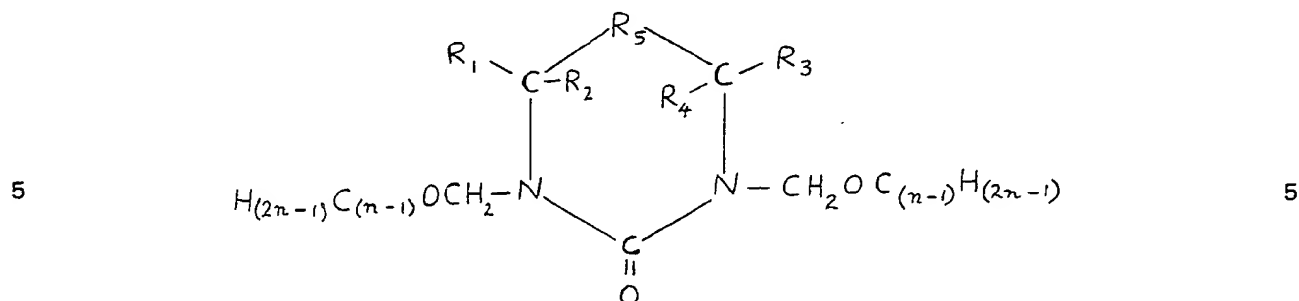
The present invention provides a process for flameproofing a textile fabric comprising cellulosic fibres which process comprises impregnating the textile fabric with an aqueous solution at a pH of 4 to 8 which contains a compound containing the THP ion, a carbamic acid derivative and a di-functional nitrogen-containing reactant compound, which cannot form a thermoset resin when heated alone, the amount of tetrakis hydroxymethyl phosphonium ion on the fabric being 15—30% based on the weight of the fabric, then drying the impregnated fabric and heating it so as to form a polymer system derived from the THP ion, the carbamic acid derivative and the difunctional nitrogen-containing reactant compound.

This process may be applied to textiles of any weight e.g. 100—400 g/m<sup>2</sup> containing cellulosic fibres such as cotton, linen and viscose rayon, including mixtures of cellulosic fibres with each other or with synthetic textile fibres such as polyester, polyamide and acrylic fibres e.g. with weight proportions of synthetic textile fibres to cellulosic textile fibres of up to 4:1 e.g. 0.1—4:1 preferably 1:3—3:1 and especially 4:6 to 7:3. It is particularly suitable for use on mixtures of polyester and cellulosic fibres such as fabrics in which the weight ratio of polyester to cellulose is between 0.25:1 and 2.5:1 e.g. 50/50 and 67/33 polyester-cotton fabrics.

The difunctional reactant compound is one which is capable of reacting with THP ion and cellulose on heating in the presence of an acid catalyst, but which does not react with itself to form a thermoset resin e.g. by heating at 150°C. Compounds of this type known as "reactant resins" are widely used in the textile trade to impart crease-resistant finishes to textiles, see for example "Self-Smoothing Fabrics" by J. T. Marsh from page 64. The difunctional nitrogen-containing reactant compound is usually a compound having at least two nitrogen atoms wherein there are no hydrogen atoms attached to nitrogen atoms and there are two nitrogen atoms each attached to an optionally etherified methylol group of formula  $\text{—CH}_2\text{OC}_{(n-1)}\text{H}_{(2n-1)}$  where n is positive integer, preferably 1—5, more preferably 1—3 especially 1. It is generally a heterocyclic compound in which the said two nitrogen atoms form part of the same heterocyclic ring. Preferably each of the said two nitrogen atoms is joined to a carbonyl group, especially with both nitrogen atoms joined to the same carbonyl group so that the heterocyclic compound contains a grouping of formula



wherein n is as defined above, and the nitrogen atoms and the carbon atoms of the carbonyl group form part of the heterocyclic ring of 5 or 6 ring atoms. Preferably the di-functional nitrogen containing compound is of formula



wherein n is defined, above each of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$ , which is the same or different represents a hydrogen atom, an alkyl group of 1—4 carbon atoms, e.g. methyl, or a hydroxyl group.  $R_5$  is a single bond or a divalent alkylene or alkylidene group of 1—6 carbons, or a group  $NR_6$  where  $R_6$  is an alkyl group of 1—6 carbon atoms, particularly ethyl. Particularly  $R_3$  and  $R_1$  are hydrogen atoms and  $R_2$  and  $R_4$  are both hydrogen or hydroxyl; preferably  $R_5$  is a single bond (as in ethylene urea derivatives) or a methylene group (as in propylene urea derivatives) or an  $NR_6$  group (as in triazones). So preferred compounds are cyclic reactants of the triazone or cyclic urea types such as dimethylol alkyl triazones e.g. dimethylol ethyl triazone or preferably dimethylol cyclic alkylene ureas e.g. dimethylol propylene urea, dimethylol ethylene urea and especially dihydroxy dimethylol ethylene urea, a compound of the above formula in which  $n=1$ ,  $R_1$  and  $R_2$  are hydrogen,  $R_3$  and  $R_4$  are hydroxyl and  $R_5$  is a single bond. Esterified nitrogen containing compounds may be the methyl, ethyl, isopropyl or any butyl ether of the above compounds. The THP compound may be THPOH or preferably any water soluble THP salt. The salt may, for example, be the formate, acetate, phosphate or sulphate or a halide such as the chloride. The solution is at pH 4—8, usually at an acid pH e.g. 4—6.5 but preferably 5—6 e.g. 5.5. THPOH is the name given to a neutralised THP salt so that above pH 7.0 the THP salt may be considered to be present largely as THPOH. The pH is adjusted, if necessary to the desired figure by addition of a water soluble base, which may be in organic such as an alkali metal hydroxide, phosphate, carbonate or bicarbonate such as sodium hydroxide, disodium phosphate or sodium carbonate but is preferably organic such as a tertiary amine of formula  $(R_7)_3N$ , where each  $R_7$  group is an alkyl or preferably hydroxyalkyl group each of 1—4 carbon atoms; preferably the base is an alkanolamine e.g. triethanolamine. An acid catalyst may optionally be added, preferably a salt which is a Lewis acid such as a metal halide such as magnesium chloride or a zinc salt such as zinc nitrate. This use of an acid catalyst is especially preferred when THPOH is used i.e. at high pH.

The carbamic acid derivative is one which is capable of reaction with THP to form a condensate particularly one with 2 nitrogen atoms each with at least one hydrogen atom attached thereto and especially one free of methylol groups. The carbamic acid derivative may be for example, a compound of the formula  $XC(NH_2)NHY$  wherein X represents O, or S, or NH and Y represents H or CN such as urea, thiourea, guanidine or dicyandiamide. Urea is preferred and will be exemplified as the carbamic acid derivative hereafter.

The THP compound provides the phosphorus required to impart flame retardant properties. The reactant compound fixes the THP to the cellulose. If it is omitted very little solid fixation is obtained, and the fabric shows no flame retardant properties. The urea contributes towards the formation of the polymer system, introducing more nitrogen, linking the THP components together, but not linking to the cellulose. When used in excess, however, urea reduces the durability of the polymer produces to repeated washing.

Both the urea and the reactant compound react with the THP, and it is convenient to express the proportions of the three components in terms of molar proportions of urea and reactant compound to THP ion respectively. The preferred ranges are urea:THP 0.2—1.5:1 such as 0.4—1.2:1 e.g. 0.5—1.2:1 preferably 0.5—1.0:1 such as 0.7:1, Reactant compound:THP 0.1—0.8:1 e.g. 0.15—0.6:1 preferably 0.35:1, Urea:Reactant compound 1—12:1 e.g. 1.5—6:1 preferably 2—3:1.

The objects are to fix as much THP as possible on the fibres, so as to produce the maximum flameproofing effect, using a minimum of two nitrogen compounds to achieve this end and to secure as much cross-linking of the polymer as possible. The effect of varying the proportions of the constituents of the treating bath is illustrated by certain of the Examples below.

Other textile processing aids such as wetting agents and fabric softeners may also be present in the impregnation solution, generally in amounts up to 3% by weight of the solution.

The cellulosic fabric may be impregnated with the solution and squeezed to give the required pick-up. The amount of THP ion applied to the fabric is 15—30% by weight e.g. 16—25% or 17—23% or 20—25% on the weight of the fabric. With 100% cotton fabrics the amount of THP ion is preferably 17—23% by weight and with polyester/cotton mixtures of 1:3 to 3:1 weight ratios, the amount of THP ion is preferably 17.5—25 by weight. The fabric may then be dried and cured at an elevated temperature. During the curing the THP reacts with the urea and reactant compound and it is believed that the cellulose is cross-linked to a polymer having repeated units derived from all 3 compounds. After the heat cure the cured fabric does not require further curing by treatment with ammonia; preferably there is no subsequent treatment of the cured fabric with ammonia in which case the cured fabric is not further curable with ammonia. The cured fabric may be washed with an oxidising agent.

In summary, the process of the invention preferably comprises the following steps:—

- 1) The treatment solution is prepared by dissolving the THP compound, carbamic acid derivative, reactant compound, and if needed, base in water, in the required proportions. The solution may also contain additional textile processing aids, such as wetting agents or fabric softeners.
  - 2) The fabric is impregnated in the treatment solution, and squeezed to give the required pick-up.
  - 3) The fabric is dried (e.g. by heating at 80—100°C for 1—20 minutes).
  - 4) The fabric is cured at an elevated temperature usually of 80—215°C, preferably 140—190°C, with cure times of 1—10 minutes. Typical curing conditions are 2—6 e.g. 3—5 minutes at 150°C, but shorter times at higher temperature, or longer times at lower temperatures, may be used.
- Drying and curing may be combined in a single operation. After the curing operation the fabric is washed preferably employing an oxidising agent, such as hydrogen peroxide.

The four-component treatment solution is unstable during transport and storage. We have found that if the THP compound and carbamic acid derivative are made up in one solution and the reactant compound and base in another, both solutions are more stable. It is thus possible to sell the formulation as a two-part product, to be combined by the user.

The present invention also provides a two pack system for use in a textile flameproofing process, said system comprising in pack (a), an aqueous solution of a compound containing the tetrakis(hydroxymethyl) phosphonium ion and a carbamic acid derivative and in pack (b) an aqueous solution of a di-functional nitrogen-containing reactant compound which cannot form a thermoset resin when heated alone, and a base. The quantity of the THP ion and said base are usually such that the solution obtained on mixing the total contents of packs (a) and (b) has a pH of 4—8 and has 10—50% e.g. 15—40 20—40% (wt) THP ion. The solutions are kept in the packs, which may be drums or bottles. A THP compound/carbamic acid derivative solution can usefully contain 30—65% THP ion by weight. It is convenient to adjust the strength of this solution to contain a certain quantity of THP compound in moles/l or moles/kg. The strength of the reactant/base solution can then be adjusted on the same basis so that the correct ratio of components can be obtained by using a given ratio of the two solutions by volume or by weight. The solution ready for impregnating the fabric preferably contains 20—40% by weight e.g. 24—34% by weight THP ion.

The THP compound and carbamic acid derivative may be heated together so as to promote the formation of a precondensate, but this is not necessary and is not recommended because it gives a firmer handle to the treated fabric.

The invention is illustrated by the following Examples 1—30 with Comparative Examples A—S in which all proportions are in parts by weight unless otherwise stated:—

#### Example 1

Two solutions were prepared as follows:—

#### Solution A

170 parts urea were dissolved in 200 parts water and then mixed with a solution containing 600 parts of tetrakis hydroxymethyl phosphonium chloride (THPC) in 150 parts of water.

#### Solution B

120 parts triethanolamine were mixed into a solution containing 184 parts of dimethylol dihydroxy ethylene urea in 216 parts of water.

Solutions A and B showed no signs of instability, but six days after mixing together solid began to separate from the combined solution.

A 50/50 polyester cotton duck fabric weighing 300 g/m<sup>2</sup> was padded through a solution of pH 4.85 containing 1120 parts of solution A and 520 parts of solution B mixed immediately before use. The wet pick-up obtained was 75%, giving a 27.4% THPC add-on (22.3% THP ion).

The fabric was dried for 5 minutes at 95°C and then cured for 3 minutes at 150°C. It was then washed in a solution containing 5 ml/l nonionic detergent and 10 ml/l H<sub>2</sub>O<sub>2</sub> (35%) for 10 minutes cold followed by 20 minutes at 60°C, rinsed thoroughly and dried. The treated fabric showed a weight increase of 21.1%, gave an average char length of 3.8" when tested by BS3119, and an oxygen index of 27.6%. (The oxygen index is the minimum % oxygen needed to just sustain combustion when tested in a Limiting Oxygen Index apparatus as described in ASTM D28670. The same fabric when treated

with 27.2% THPC in the form of a THPC-urea precondensate, dried, ammonia cured, and washed off as above, gave a weight increase of 10.6%, burnt completely when tested by BS3119 and gave an oxygen index of 24.4% (oxygen index of untreated fabric 18.8).

#### Example 2

- 5 A 67/33 polyester-cotton drill fabric weighing 190 g/m<sup>2</sup> was treated as described in Example 1. 5  
The wet pick-up was 64.8% giving a 23.7% THPC add-on (19.3% THP ion). The final weight increase was 22.2%, the average char length was 5.2", and the oxygen index was 27.4%, (untreated fabric 18.8%).

#### Example 3

- 10 A 100% cotton drill fabric weighing 280 g/m<sup>2</sup> was treated as described in Example 1, but diluting 10  
every 100 parts of the combined solutions A & B with 20 parts of water. The wet pick-up was 79.6% giving a 24.3% THPC add-on (19.7% THP ion). The final weight increase was 15.0%, the average char length 2.4", and the oxygen index 35.9% (untreated fabric 18.5%).

#### Example 4

- 15 Solution C was prepared as solution B in Example 1, but using only 60 parts of triethanolamine 15  
instead of 120 parts. Solutions A and C were mixed in the ratio 800:368 and 60 parts of an anionic softening agent and 6 parts of a nonionic wetting agent were added. A 67/33 polyester-cotton fabric as in Example 2 was padded in this solution giving a wet pick-up of 63.0% and a THPC add-on of 21.9%. The solution was then diluted in the ratio 617 parts to 103 parts of water, and a cotton drill  
20 fabric as in Example 3 was padded in the diluted solution, giving a wet pick-up of 72.1% and a THPC 20  
add-on of 21.4% (17.4% THP). The two fabrics were dried, cured and washed off as in Example 1.

The results obtained were as follows:—

|    |   | <i>polyester/cotton</i> | <i>all cotton</i> |    |
|----|---|-------------------------|-------------------|----|
| 25 | final weight increase, %                                | 26.7                    | 23.5              |    |
|    | average char length, as finished, inches                | 4.0                     | 2.3               | 25 |
|    | average char length, after washing to<br>BS3120, inches | 4.2                     | 2.1               |    |
|    | crease recovery warp and weft                           | 224                     | 252               |    |
|    | handle  | good                    | good              |    |

- 30 The crease recovery angle is the sum of the warp and weft results as described by the Monsanto 30  
crease recovery method.

#### Example 5 and 6 and Comparative Examples A—F

A series of solutions were prepared containing various combinations of the following components in a total of 1000 parts:—

|    |   |                                     |    |
|----|---|-------------------------------------|----|
| 35 | THPC                                    | 300 parts                           | 35 |
|    | Urea                                    | 85 parts (0.90 moles per mole THPC) |    |
|    | Dihydroxydimethylethylene urea (DHDMEU) | 92 parts (0.33 moles per mole THPC) |    |
|    | Triethanolamine (TEA)                   | 60 parts (0.25 moles per mole THPC) |    |

- 40 Cotton drill fabric was padded in these solutions to give approx. 74% wet pick-up (22.2 THPC 40  
add-on i.e. 18.0% THP ion), and dried, cured and washed off as in Example 1. A further sample was treated with a solution of all four components in which the solution of THPC and urea had been  
refluxed for 1 hour in order to form a THPC-urea precondensate.

The results obtained were as follows:—

| Ex. | Bath components                     | % Final weight increase | char length in inches as finished | char length in inches after washing | oxygen index | weft tear strength g |
|-----|-------------------------------------|-------------------------|-----------------------------------|-------------------------------------|--------------|----------------------|
| A   | (untreated fabric)                  |                         | BC                                | BC                                  | 18.5         | 2080                 |
| B   | THPC+urea+TEA                       | 0                       | BC                                | BC                                  | 17.8         | 2464                 |
| C   | THPC+urea                           | 1.7                     | BC                                | BC                                  | 20.6         | 2368                 |
| D   | THPC+DHDMEU+TEA                     | 7.2                     | BC                                | BC                                  | 22.6         | 2240                 |
| E   | THPC+DHDMEU                         | 11.3                    | BC                                | BC                                  | 22.8         | 1024                 |
| 5   | THPC+DHDMEU+urea+TEA                | 16.0                    | 2.6                               | 2.7                                 | 35.3         | 2112                 |
| F   | THPC+DHDMEU+urea                    | 19.1                    | 2.6                               | 2.7                                 | 36.5         | 1120                 |
| 6   | THPC-urea precondensate +DHDMEU+TEA | 18.6                    | 2.3                               | 2.5                                 | 35.2         | 1088                 |

BC indicates "burnt completely".

**Example 7—10, Comparative Ex. G, H**

A cotton drill fabric was treated as in Example 5, omitting urea from the treatment bath. The treatment was repeated using increasing additions of urea to the initial solution, so that the urea:THP molar ratio increased over the range 0—2.2:1. The final solid add-on increased from 10.2 to 26.7 and the fabric handle became progressively stiffer as the proportion of urea was increased. The treated fabrics were then washed for 6 hours at the boil in 2 g/l soap and 2 g/l soda ash, when the fabrics treated with solutions containing 0.5 or 0.7 moles urea/mole THP gave the best overall finish retention.

|    | Ex. | Molar ratio<br>urea:THP | % Solid add-on<br>As finished | % Solid add-on<br>After washing | % Washing<br>Loss |    |
|----|-----|-------------------------|-------------------------------|---------------------------------|-------------------|----|
| 10 | G   | 0                       | 10.2                          | 7.2                             | 42                | 10 |
|    | 7   | 0.5                     | 16.8                          | 13.6                            | 20                |    |
|    | 8   | 0.7                     | 19.4                          | 14.5                            | 25                |    |
|    | 9   | 0.9                     | 21.1                          | 12.8                            | 34                |    |
|    | 10  | 1.2                     | 23.6                          | 13.5                            | 43                |    |
| 15 | H   | 2.2                     | 26.7                          | 6.7                             | 75                | 15 |

**Example 11—13, Comparative Ex. J—L**

A cotton drill fabric was treated as in Example 5, omitting the DHDMEU from the treatment bath. The treatment was repeated using increasing additions of DHDMEU to the initial solution, so that the DHDMEU:THP molar ratio increased over the range 0—1.05:1. The final solid add-on increased from 4.7 to 28.0% and the fabric handle became progressively stiffer as the proportion of DHDMEU was increased. With DHDMEU:THP molar ratios in excess of 0.35:1 the weight increase appears to be accounted for by fixation of the DHDMEU itself, and no increase in the fixation of the other components is obtained.

|    | Ex. | Molar ratio<br>DHDMEU:THP | % solid add on<br>(As finished) | (% solid add-on<br>As finished)—<br>(theoretical<br>DHDMEU pickup) |    |
|----|-----|---------------------------|---------------------------------|--|----|
| 25 | J   | 0                         | 4.7                             | 4.7  | 25 |
|    | 11  | 0.16                      | 15.6                            | 11.4   |    |
| 30 | 12  | 0.35                      | 22.4                            | 14.6   | 30 |
|    | 13  | 0.56                      | 23.0                            | 11.9   |    |
|    | K   | 0.79                      | 25.8                            | 11.4   |    |
|    | L   | 1.05                      | 28.0                            | 11.1   |    |

**Example 14—18 and Comparative Ex. M/N**

A cotton drill fabric was treated as in Example 5, omitting the triethanolamine from the treatment bath. The treatment was repeated using increasing additions of TEA to the initial solution, so that the TEA:THP molar ratio increased over the range 0—0.62:1 and the pH of the solution varied from 2.4 to 6.1. The final solid add-on remained virtually the same but the tear strength of the treated fabrics increased as the proportion of TEA was increased.

| 40 | Results |   |      |                   |                          | 40 |
|----|---------|---|------|-------------------|--------------------------|----|
|    | Ex.     | Molar ratio<br>TEA:THPC<br>(untreated fabric) | pH   | % solid<br>add-on | Weft Tear<br>strength, g |    |
|    | M       | untreated fabric                              | —    | —                 | 2200                     |    |
| 45 | N       | 0   | 2.4  | 23.7              | 256                      | 45 |
|    | 14      | 0.12  | 4.8  | 24.8              | 704                      |    |
|    | 15      | 0.24  | 5.4  | 22.4              | 1088                     |    |
|    | 16      | 0.37  | 5.65 | 21.3              | 1264                     |    |
|    | 17      | 0.48  | 5.9  | 23.5              | 1248                     |    |
| 50 | 18      | 0.62  | 6.1  | 20.4              | 1568                     | 50 |

**Examples 19—22, Comparative Examples P, Q**

Treatment baths were prepared as follows:—

|    |                 | Bath D | E     | F     |    |
|----|-----------------|--------|-------|-------|----|
| 55 | THPC (100%)     | 250 g  | 320 g | 280 g | 55 |
|    | NaOH            | 25 g   | 32 g  | 0     |    |
|    | triethanolamine | 0      | 0     | 54 g  |    |
|    | Urea            | 50 g   | 64 g  | 62 g  |    |
|    | DHDMEU          | 70 g   | 88 g  | 90 g  |    |

|  | <i>Bath D</i> | <i>E</i> | <i>F</i> |   |
|--|---------------|----------|----------|---|
| Polyethylene softener                      | 20 g          | 20 g     | 20 g     |   |
| Nonionic wetting agent                     | 1 g           | 1 g      | 1 g      |   |
| water to                                   | 1000 ml       | 1000 ml  | 1000 g   |   |
| 5 % THP <sup>+</sup> content (by analysis) | 18.0          | 22.0     | 23.4     | 5 |
| Specific Gravity                           | 1.122         | 1.157    | 1.165    |   |
| pH   | 6.5           | 6.1      | 5.2      |   |

10 Samples of 50/50 polyester cotton sheeting (129 g/m<sup>2</sup>) and 100% cotton drill (280 g/m<sup>2</sup>) were padded in these solutions, dried, cured and washed off and tested as in Example 1. The results are summarised in the following table. 10

|                               | <i>bath D</i> | <i>Polyester/cotton</i> |          | <i>Cotton</i> |          |          |    |
|-------------------------------|---------------|-------------------------|----------|---------------|----------|----------|----|
| Example                       | Comp. P       | <i>D</i>                | <i>F</i> | Comp. Q       | <i>E</i> | <i>F</i> |    |
| % Wet pick-up                 | 81.7          | 78.0                    | 79.4     | 79.9          | 79.2     | 79.4     |    |
| 15 % THP <sup>+</sup> pick-up | 14.7          | 17.2                    | 18.6     | 14.4          | 17.4     | 18.6     | 15 |
| % Final add-on                | 13.0          | 18.4                    | 24.2     | 9.0           | 25.6     | 29.4     |    |
| Char length BS3119            | BEL           | 3.7''                   | 3.4''    | 2.6''         | 1.8''    | 2.1''    |    |

BEL means burns entire length.

#### Examples 23—28

20 Treatment baths G and H were prepared as follows. 20

|    |                            |  |    |
|----|----------------------------|--|----|
|    | THPC (100%)                | 368 g  |    |
|    | urea                       | 80 g (0.7:1 mole per mole THP <sup>+</sup> )   |    |
|    | DHDMEU                     | 118 g (0.35:1 mole per mole)                   |    |
| 25 | Polyethylene softener      | 20 g   |    |
|    | non-ionic wetting agent    | 1 g  |    |
|    | bath G triethanolamine     | 70 g (0.251:1 mole per mole THP <sup>+</sup> ) | 25 |
|    | bath H NaOH                | 19 g (0.25:1 mole per mole THP <sup>+</sup> )  |    |
|    | water to 1000 g total bath |  |    |

30 Samples of 100% cotton drill fabric (280 g/m<sup>2</sup>) were padded in the above solutions, dried, cured, washed off and tested as in Example 1. The baths were then progressively diluted with water and the treatments repeated. The results are summarised in the following table. 30

|                              | <i>Bath G</i> |               |           | <i>Bath H</i> |               |           |    |
|------------------------------|---------------|---------------|-----------|---------------|---------------|-----------|----|
| <i>Example</i>               | <i>23</i>     | <i>24</i>     | <i>25</i> | <i>26</i>     | <i>27</i>     | <i>28</i> |    |
| % THP <sup>+</sup> in bath   | 25.3          | 23.0          | 20.9      | 25.1          | 22.9          | 20.8      |    |
| 35 % wet pick-up             | 84.6          | 83.7          | 82.2      | 84.9          | 82.3          | 81.8      | 35 |
| % THP <sup>+</sup> on fabric | 21.4          | 19.3          | 17.2      | 21.3          | 18.8          | 17.0      |    |
| Final add-on %               | 21.4          | 17.6          | 16.0      | 18.3          | 17.1          | 13.0      |    |
| Char length ins.             | 210           | 2.1           | 2.4       | 2.0           | 2.2           | 2.5       |    |
| Char length after            |               |               |           |               |               |           |    |
| 40 12 washes ins.            | 1.7           | 2.0           | 2.2       | 1.8           | 1.9           | 3.1       | 40 |
| handle                       | firm          | slightly firm | soft      | firm          | slightly firm | soft      |    |

#### Example 29 and 30. Comparative Examples R and S

Treatment baths J and K were prepared as follows

|    |                            |   |    |
|----|----------------------------|---|----|
| 45 | THPC (100%)                | 280 g   | 45 |
|    | urea                       | 62 g (0.7 moles per mole THP <sup>+</sup> )   |    |
|    | Triethanolamine            | 54 g (0.25 moles per mole THP <sup>+</sup> )  |    |
|    | Bath J DHDMEU              | 92 g (0.35 moles per mole THP <sup>+</sup> )  |    |
| 50 | Bath K dimethyl ether      | 126 g (0.35 moles per mole THP <sup>+</sup> ) | 50 |
|    | of trimethylolmelamine     |   |    |
|    | Water to 1000 g total bath |   |    |

Sample of 100% cotton drill and 50/50 polyester cotton sheeting (both as in Ex. 19) were padded in these solutions, dried, cured and washed off and tested as in Example 1. The results are summarised in the following table.

|    | <i>Fabric<br/>Bath</i>       | <i>Polyester/cotton</i> |          | <i>Cotton</i>    |              |
|----|------------------------------|-------------------------|----------|------------------|--------------|
|    |                              | <i>J</i>                | <i>K</i> | <i>J</i>         | <i>K</i>     |
|    | Example                      | 29                      | R        | 30               | S            |
| 5  | % THP <sup>+</sup> in bath   | 22.8                    | 22.8     | 22.8             | 22.8         |
|    | % wet pick-up                | 82.8                    | 84.4     | 80.3             | 83.3         |
|    | % THP <sup>+</sup> on fabric | 18.9                    | 19.2     | 18.3             | 19.0         |
|    | % final add-on               | 26.1                    | 29.9     | 17.5             | 27.0         |
| 10 | Char length (ins)            | 3.1                     | 3.0      | 2.2              | 1.8          |
|    | handle                       | slightly<br>firm        | firm     | slightly<br>firm | very<br>firm |

### Claims

1. A process for flameproofing a textile fabric comprising cellulosic fibres which process comprises impregnating the fabric with an aqueous solution at a pH not exceeding 8 which contains a compound containing the tetrakis hydroxymethyl phosphonium ion, a carbamic acid derivative and a difunctional nitrogen-containing reactant compound, which cannot form a thermoset resin when heated alone, the amount of Tetrakis (hydroxymethyl) phosphonium ion on the fabric being 15—30% based on the weight of the fabric, then drying the impregnated fabric and heating it so as to form a polymer system derived from the tetrakis hydroxymethyl phosphonium ion, the carbamic acid derivative and the difunctional nitrogen-containing reactant compound. 15
2. A process according to claim 1 in which the fabric is a mixture of cellulosic fibres with synthetic textile fibres. 20
3. A process according to claim 2 in which the fabric is a mixture of polyester and cellulosic fibres in a weight ratio of 0.25:1 to 2.2:1.
4. A process according to any one of the preceding claims in which the reactant compound is a compound with two —N—CH<sub>2</sub>OH groups. 25
5. A process according to claim 4 in which the reactant compound is a heterocyclic compound containing at least two nitrogen ring atoms and two nitrogen ring atoms are each joined to a methylol group and also to a carbonyl group.
6. A process according to claim 5 in which the reactant compound is a dimethylol alkyl triazone.
7. A process according to claim 5 in which the reactant compound is a dimethylol cyclic alkylene urea. 30
8. A process according to any preceding claim in which the compound containing the tetrakis hydroxymethyl phosphonium ion is the chloride.
9. A process according to any preceding claim in which the carbamic acid derivative is urea.
10. A process according to claim 9 in which the molar proportion of urea to tetrakis hydroxymethyl phosphonium ion is between 0.4:1 and 1.2:1. 35
11. A process according to any preceding claim in which the molar proportion of reactant compound to tetrakis hydroxymethyl phosphonium ion is between 0.15:1 and 0.6:1.
12. A process according to any preceding claim in which the pH is adjusted by addition of a water soluble organic base. 40
13. A process according to claim 12 in which the base is triethanolamine.
14. A process according to claim 1 substantially as described in any one of Examples herein.
15. A textile fabric flameproofed by a process as claimed in any one of the preceding claims.
16. A two pack system for use in a textile flameproofing process as claimed in any one of the claims 1—14 said system comprising in pack (a) in aqueous solution of a compound containing the tetrakis hydroxymethyl phosphonium ion and a carbamic acid derivative and in pack (b) aqueous solution of a difunctional nitrogen-containing reactant compound which cannot form a thermoset resin when heated alone, and a base, the quantity of the said tetrakis hydroxymethyl phosphonium ion and said base being such that the solution obtained on mixing the total contents of pack (a) and (b) has a pH not exceeding 8 and a tetrakis hydroxymethyl phosphonium ion concentration of 10—50% by weight. 45
17. A system according to claim 16 in which component solution (b) comprises dimethylol dihydroxy ethylene urea and triethanolamine.
18. A system according to claim 16, wherein pack (a) comprises an aqueous solution of tetrakis hydroxymethyl phosphonium chloride and urea. 55
19. A system according to claim 16, 17 or 18 in which the concentration in the solution in pack (a) of the compound containing the tetrakis hydroxymethyl phosphonium ion is 40—80% by weight.